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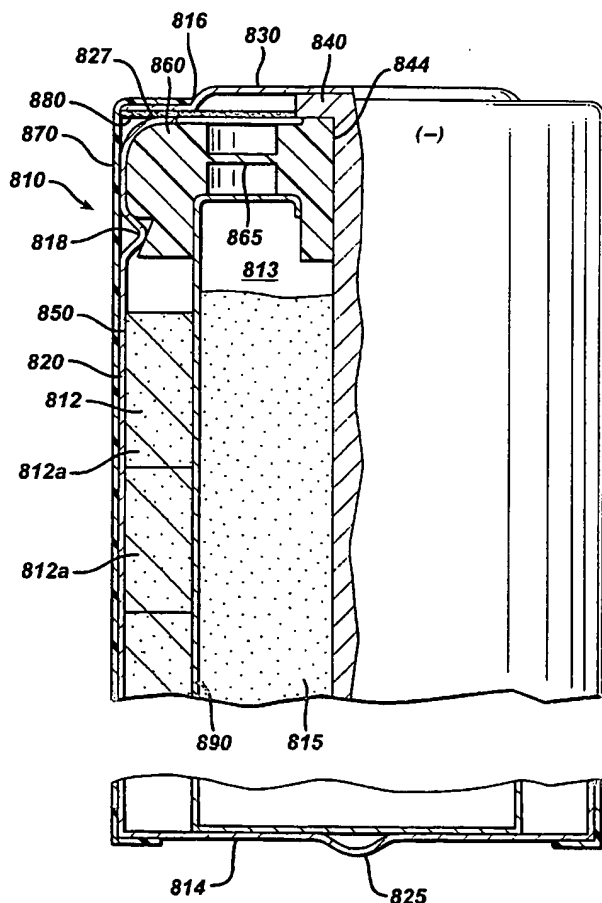
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(54) Title: **ALKALINE CELL WITH IMPROVED ANODE**



(57) Abstract: A method of forming an anode comprising zinc for an alkaline cell. The method involves mixing zinc particles with binders including preferably polyvinylalcohol, surfactant and water to form a wet paste. The wet paste is molded into the near shape of the cell's anode cavity and then heated to evaporate water. A solid porous zinc mass is formed having microscopic void spaces between the zinc particles. The solid mass can be inserted into the cell's anode cavity and aqueous alkaline electrolyte, preferably comprising potassium hydroxide, then added. The solid mass absorbs the aqueous electrolyte and expands to fill the anode cavity to form the final fresh anode.

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ALKALINE CELL WITH IMPROVED ANODE

This invention relates to zinc anode for an alkaline cell. The invention relates to an anode prepared by preforming a solid porous mass comprising zinc particles to which aqueous alkaline electrolyte is added to form the final anode.

5 Conventional alkaline electrochemical cells have an anode comprising zinc and a cathode comprising manganese dioxide. The cell is typically formed of a cylindrical casing, but casings having flat surfaces or disk type button cells are also possible. The casing is initially formed with an enlarged open end and opposing closed end. After the cell contents are supplied, an end cap with insulating plug is inserted into
10 the open end. The cell is closed usually by crimping the casing edge over an edge of the insulating plug and radially compressing the casing around the insulating plug to provide a tight seal. An end cap plate in electrical contact with the anode can be attached over the plug to form the negative terminal. A portion of the cell casing at the opposing closed end forms the positive terminal.

5 Primary alkaline electrochemical cells typically include an anode comprising zinc anode active material, an alkaline electrolyte, a cathode comprising manganese dioxide cathode active material, and an electrolyte permeable separator film between the anode and cathode. (Anode active material is defined herein as anode material which undergoes useful electrochemical reaction upon cell discharge.) The
10 separator may typically be of cellulose or cellulosic and polyvinylalcohol fibers. The anode active material can include for example, zinc particles admixed with conventional gelling agents, such as sodium carboxymethyl cellulose or the sodium salt of an acrylic acid copolymer, and an electrolyte. The gelling agents, which become activated upon contact with alkaline electrolyte, serve to suspend the zinc particles in a gelled medium
15 and to maintain them in contact with one another. Typically, a conductive metal nail inserted into the anode active material serves as the anode current collector, which is electrically connected to the negative terminal end cap. The electrolyte can be an aqueous solution of an alkali metal hydroxide for example, potassium hydroxide, sodium hydroxide or lithium hydroxide. The cathode typically includes particulate
20 manganese dioxide as the electrochemically active material admixed with an electrically conductive additive, typically graphite material, to enhance electrical conductivity. Optionally, polymeric binders, and other additives, such as titanium-containing compounds can be added to the cathode.

5 Zinc anodes for alkaline cells are conventionally prepared in the form of a slurry which is pumped into the cell's anode cavity. The slurry is typically prepared by

forming a gelled electrolyte mixture comprising an aqueous alkaline electrolyte, preferably a gelled aqueous potassium hydroxide. Such gelled electrolyte can be formed, for example, by mixing a gelling agent such as a polyacrylic acid gelling agent with aqueous alkaline electrolyte. A zinc powder blend containing a small amount of surfactant is then typically mixed into gelled electrolyte to form an anode slurry mixture. The anode slurry mixture is conventionally pumped into the cell's anode cavity by a slurry pump. Although the slurry pump is designed to keep air from entering the slurry mixture, the pump nevertheless typically allows small amounts of air to enter the slurry as it is pumped into the cell's anode cavity. This causes small air pockets to develop within the anode mixture pumped into the cell's anode cavity. Such air pockets can be microscopic in size but more typically there are a number of such air pockets which are visible to the naked eye when the anode is examined by simple X-ray photography without magnification. Optionally some additional aqueous electrolyte may be added to adjust the electrolyte composition in the anode mixture after the slurry is pumped into the anode cavity. However, such additional electrolyte does not noticeably reduce the number of air pockets within the anode slurry. The presence of such air pockets within the anode slurry tends to reduce the overall conductivity of the anode because it reduces the level of zinc interparticle contact in the region of the air pockets.

In a commercial cell assembly line such zinc slurry tends to plug the dispensing tube, leading to down time of the assembly line. Also, the storage of large batches of the slurry tends to result in settling or precipitation of some of the zinc particles over time, which can result ultimately in a non-uniform distribution of zinc particles. The zinc particle settling or precipitation could also occur from the gelled zinc slurry already dispensed into the cells, for example, in cases where the cells are stored for long time or experience some shock or vibration. Such precipitation of the zinc particles will cause non-uniform distribution of the zinc within the anode and subsequent loss of electrical continuity. Also pumping the anode slurry into very small dimensioned, particularly, small irregular shaped anode cavities becomes difficult. In such case the slurry mixture must be prepared with more attention given to zinc particle shape and slurry flowability (consistency) which can compromise the final anode from the standpoint of overall conductivity. In small size cells, for example, miniature button cells, the anode can be prepared by dispensing a mixture of discrete zinc particles and gelling agent into cell's anode cavity and the adding aqueous alkaline electrolyte to form the gelled anode. In commercial production this becomes an inefficient and speed

limited method of forming the anode for zinc/air cells. It can also lead to nonuniform dispersion of zinc particles within the gelled anode.

The manganese dioxide used in the cathode is preferably electrolytic manganese dioxide (EMD) which is made by direct electrolysis of a bath of manganese sulfate and sulfuric acid. The EMD is desirable since it has a high density and high
5 purity. The resistivity of EMD is fairly low. An electrically conductive material is typically added to the cathode mixture to improve the electric conductivity between individual manganese dioxide particles. Such electrically conductive additive also improves electric conductivity between the manganese dioxide particles and the cell
0 housing, which also serves as cathode current collector. Suitable electrically conductive additives can include, for example, conductive carbon powders, such as carbon blacks, including acetylene blacks, flaky crystalline natural graphite, flaky crystalline synthetic graphite, including expanded or exfoliated graphite. The resistivity of graphites such as flaky natural or expanded graphites can typically be between about 3×10^{-3} ohm-cm and
5 4×10^{-3} ohm-cm.

It is desirable to eliminate the need for preparing the anode as a zinc slurry mixture. Rather, it is desired to prepare the anode in preformed solid form which can be inserted as a dry solid into the anode cavity without the need of pumping a slurry mixture into the anode cavity.

The invention is directed to a method of forming an anode comprising
10 zinc for an alkaline cell. The method of forming the anode of the invention is suitable for preparing zinc anodes for alkaline cells, particularly primary (nonrechargeable) alkaline cells. Such cells typically have an anode comprising particulate zinc, a cathode comprising manganese dioxide and aqueous alkaline electrolyte, preferably comprising potassium hydroxide. The method of the invention may also be used to prepare anodes
15 comprising particulate zinc in alkaline cells having cathodes other than manganese dioxide, provided such cells employ aqueous alkaline electrolyte, for example, comprising aqueous potassium hydroxide. The method of the invention can be used in preparing zinc anodes for alkaline cells regardless of the cells overall shape. For
20 example, the cell may be a cylindrical cell, button cell or flat cell, provided the cell employs aqueous alkaline electrolyte. The anode of the invention can be used regardless of the shape of the alkaline cell's anode cavity. For example, the anode of the invention is suitable for use in irregularly shaped anode cavity such as that disclosed in U.S.
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The method of the invention can be also used in preparing zinc anodes which are suitable for use in zinc/air cells. Such cells typically employ an anode comprising particulate zinc and aqueous alkaline electrolyte, usually comprising potassium hydroxide. Such zinc/air cells are commonly employed in the form of button cells used, for example, in hearing aids. Zinc/air cells may also be in the form of elongated cylindrical cells. Zinc/air cells are depolarized with air and typically have cathodes comprising manganese dioxide. The manganese dioxide may act as a cathode catalyst or in part as active cathode material which undergoes useful electrochemical reaction during battery discharge.

An aspect of the invention is directed to preparing an aqueous wet zinc paste and molding the paste in the approximate shape of the anode cavity for an alkaline cell. This can be done conveniently by applying the wet paste into a steel, ceramic or plastic die having a cavity therein in the approximate shape of the cell's anode cavity. The paste fills the cavity under pressure and thereby assumes the cavity shape. The paste can be pressure-molded in the die cavity under ambient temperatures for a short time, typically 2-3 seconds. The paste molded in this manner forms a wet zinc mass (wet preform) which is readily removable from the die. The wet zinc mass (wet preform) has sufficient structural integrity so that it can stand alone outside of the die while retaining its molded shape. The stand alone wet preform is then heated to evaporate water, thereby resulting in a solid, dried, porous zinc mass (solid preform) which can be stored until the cell is ready for assembly.

The wet zinc mass (wet paste) is formed as follows: A mixture of zinc particles, surfactant, hydrogel binders, polyvinylalcohol binder and water is blended into a paste using an electric/mechanical blender until the paste has a homogeneous consistency. The amount of binders and water in the blend are adjusted to control the paste consistency. Alkaline electrolyte is not added to the wet paste. The wet paste is then inserted into a cavity within a steel, ceramic, or plastic die. The die cavity has the approximate shape of the cell's anode cavity, but preferably slightly smaller. The wet paste can have a consistency much like a wet cement and thus can be conveniently extruded into the die cavity. The wet paste can be pressure-molded in the die cavity for a short period, typically about 2-3 seconds under ambient temperatures, so that it becomes compacted and fully assumes the shape of the cavity. For example, the wet paste can be filled into die cavity having the approximate shape of the desired anode cavity. The outlet end of the die cavity may abut a detachable solid base. A first stroke of a plunger can be used to compact the wet paste within the die cavity to form the compacted wet zinc mass (wet premold). The

die base can be removed and a second stroke of the plunger forces the wet zinc mass (wet premold) out from the die cavity. The binders in the wet zinc mass, particularly the polyvinylalcohol, helps to impart sufficient structural integrity to the wet mass so that it is dimensionally stabilized. The polyvinylalcohol functions as glue which holds the zinc particles together. The wet mass is dimensionally stabilized, that is, retains at least its general overall shape and can stand alone, outside of the die. The term "dimensionally stabilized" of course also extends to and includes a wet mass which completely retains the shape it obtained when formed in the mold when it is thereafter removed from the mold. Other methods of shaping the wet paste can be employed, for example, the wet paste can be inserted into an open die mold; pressure can be applied to the surface of wet paste in the mold to compact the wet paste therein to form the compacted wet zinc mass. The die mold could then be inverted to release the compacted mass. The wet zinc mass emanating from the die cavity or mold is preferably in the near shape of the anode cavity that it will be inserted into.

The wet paste forming the wet zinc mass (wet preform) comprises a mixture of zinc particles, surfactant, hydrogel binders, polyvinylalcohol binder and water. The surfactant is preferably a dinonyl phenol phosphate ester surfactant such as that available commercially under the tradename "RM-510" from Rhone-Poulenc. The binders comprises a) one or more hydrogel binders which can be in the form of commercially available gelling agents and b) a polyvinylalcohol binder. A preferred hydrogel binder is a crosslinked acrylic acid polymer gelling agent available commercially under the tradename "CARBOPOL C940" from B.F. Goodrich. The CABOPOL C940 binder may be employed alone. Preferably, however, a hydrolyzed polyacrylonitrile grafted onto a starch backbone commercially available under the tradename "Waterlock A-221" from Grain Processing Co is added to form the total hydrogel binder. The polyvinylalcohol is added to provide structural integrity to the wet paste so that it may be molded.

The wet zinc mass (wet preform) removed from the die cavity may have the following composition: zinc (80 to 94 wt.%), surfactant, e.g. dinonyl phenol phosphate ester RM-510 surfactant (0.05 to 0.2 wt.%); total binders (0.5 to 3 wt.%) comprising for example, CARBOPOL C940 binder (0.5 to 3 wt.%) and WATERLOCK A-221 binder (0.05 to 0.33 wt.%) and polyvinylalcohol (0.2 to 1 wt.%); and water (3 to 18 wt.%). The polyvinylalcohol preferably has a molecular weight between about 85000 and 146000. Such polyvinylalcohol can be obtained commercially in solid form. It can conveniently be dissolved with water before adding it to the zinc particles. The wet zinc mass (wet preform) removed from the die cavity holds at least its general overall shape when placed

on a flat surface. That is, it is dimensionally stabilized. Optionally, a separator material can be wrapped around the wet zinc mass (wet preform). The wet zinc mass may be dried by placing it in free standing form, with or without separator material wrapped around it, in an oven exposed to ambient air. The wet zinc mass, with or without separator thereon, is heated desirably at a temperature between about 55°C and 120°C, for example, at a temperature of about 55°C, to evaporate at least a portion of the water therein. It will be understood that the term dry or dried as used herein shall mean that the wet zinc mass is treated by heating and the like so that at least a portion of the free water therein is removed. Preferably, essentially all of the free water within the wet zinc mass is evaporated during the heating step thereby forming a dry, solid porous zinc mass (solid preform).

The solid porous zinc mass (solid preform) has the near shape of a cell's anode cavity. If the wet zinc mass was wrapped with separator material before drying, then the resulting solid porous zinc mass will also have the separator intact around said solid porous zinc mass and typically adhering thereto. The zinc particles are held suspended in a tight network within the dry solid mass. The solid zinc mass (solid preform) may desirably have the following composition: zinc (96 to 99 wt. %); surfactant, e.g. dinonyl phenol phosphate ester RM-510 surfactant (0.06 to 0.25 wt.%); total binders (0.5 to 3 wt.%) comprising for example, CARBOPOL C940 binder (0.5 to 3 wt.%) and WATERLOCK A-221 binder (0.05 to 0.37 wt.%) and polyvinylalcohol (0.22 to 1.2 wt.%). The solid porous zinc mass (solid preform) may have a porosity between about 25 and 50 percent, typically of between about 40 and 50 percent. (The porosity is the volume of void spaces within the mass divided by the mass overall apparent volume.) The dry solid zinc mass (solid preform) is characterized by pockets of microscopic void spaces which appear between the individual zinc particles resulting in a porosity of the solid preform of between about 25 and 50 percent, typically between about 40 and 50 percent. These microscopic void spaces were formerly filled by the water which was evaporated from the wet zinc mass (wet preform). Surprisingly, the polyvinylalcohol functions as a glue to hold the zinc particles together in a solid porous zinc mass (solid preform). The polyvinylalcohol surprisingly provides sufficient structural integrity to prevent collapse of the solid porous zinc mass (solid preform) and assures that it retains its overall shape. The solid porous zinc mass is thus dimensionally stabilized, that is, retains at least its general overall shape in free standing form. The term "dimensionally stabilized" of course also extends to and includes a mass, for example, a solid porous zinc mass which completely retains its shape when standing alone. Thus, it can be kept in storage until ready for use in the cell. During cell assembly the solid preform can be inserted into the cell's anode cavity. Then, aqueous

alkaline electrolyte, preferably comprising potassium hydroxide, is added. The solid preform immediately absorbs the aqueous alkaline electrolyte whereupon the mass preferably expands to the full shape of the anode cavity thus forming the final fresh anode. The polyvinylalcohol functions as a glue which binds the zinc particles together in both the wet zinc mass (wet preform) and the dry solid porous zinc mass (solid preform). The hydrogel binders serve mainly as gelling agents, that is, they absorb aqueous electrolyte solution and also cause expansion of the solid preform when the electrolyte solution is added thereto. The polyvinylalcohol is stable and chemically resistant to alkaline electrolyte.

The method of the invention of inserting a solid (or dimensionally stabilized) porous zinc mass into the anode cavity of an alkaline cell and then adding aqueous alkaline electrolyte thereto to form the anode thus eliminates the disadvantages associated with prior art methods of pumping a gelled anode slurry into the anode cavity or initially mixing discrete zinc particles, gelling agent and aqueous electrolyte within the anode cavity without first applying the solid porous zinc mass.

Fig. 1 is a cross-sectional cut away view of an alkaline cell having a zinc anode made by the method of the invention.

Fig. 2 is a cross sectional view of a cylindrical button cell of an alkaline cell having a zinc anode made by the method of the invention.

Fig. 3A is a drawing showing a die cavity being filled with a wet zinc paste of the invention.

Fig. 3B is a schematic showing the wet zinc mass after it has been compacted within the die cavity.

Fig. 3C is a schematic showing the compacted wet zinc mass being dried in an oven to produce a dry solid mass.

Fig. 3D is schematic showing the dry solid mass product.

Fig. 4 is a scanning electron micrograph showing the void spaces between zinc particles after water has been evaporated to form a solid porous zinc mass (solid preform).

A representative alkaline cell utilizing the anode mixture of the invention is shown in Fig.1. Alkaline cell 810 is a primary (nonrechargeable) cell. The alkaline cell 810 comprises a cylindrical casing (housing) 820 of steel, preferably nickel plated steel, having a closed end 814 and an open end 816. A premolded dry solid porous zinc mass (solid preform) 815C (Fig. 3D) is prepared and inserted into the cell's anode cavity 813 within casing 820. The solid preform is porous having a porosity, between about 25

and 50 percent, typically between about 40 and 50 percent. The solid porous zinc mass (solid preform) 815C is preferably of a hard solid consistency and is dimensionally stabilized, that is, it retains sufficient structural integrity to maintain at least its general shape outside of the cell. The solid porous zinc mass (solid preform) 815C is preferably dry and can be stored until the time of cell assembly, since the constituents therein are unreactive in a dry environment. The solid porous zinc mass 815c is preformed into the shape of the anode cavity but of somewhat smaller diameter so that it is readily insertable into the anode cavity. In a preferred embodiment the outside diameter of the solid preform 815C is selected to be between about 10 and 40 percent less than the inside diameter of the anode cavity 813 when initially inserted into said anode cavity. After the preformed solid zinc mass (solid preform) 815C is inserted into anode cavity 813, aqueous alkaline electrolyte, preferably comprising aqueous potassium hydroxide, is added to the anode cavity 813. The aqueous electrolyte is absorbed by the solid porous zinc mass which expands to the diameter and full shape of the anode cavity thus forming the final fresh anode 815.

Before the preformed solid porous zinc mass (solid preform) 815C is inserted into anode cavity 813, a cathode mixture 812 is prepared. The cathode mixture 812 contains a conductive material such as flaky crystalline natural graphite or flaky crystalline synthetic graphite including expanded graphites and graphitic carbon nanofiber and mixtures thereof. The cathode mixture 812 includes an aqueous KOH electrolyte solution and the mixture can be prepared wet, with aqueous KOH included before the mixture is inserted into the cell. For example, the casing (housing) 820 can be filled with the cathode mixture and the central portion of the cathode mixture can be excavated leaving the annular cathode 812 as shown in Fig. 1. The wet cathode mixture can be compacted while in the cell. Preferably, the cathode mixture 812 is compacted into a plurality of surface wet solid disks 812a before insertion into the cell. The cathode disks 812a are stacked one on top of the other and may then be additionally compacted while in the cell.

A separator sheet 890 can be placed against the inside surface of cathode disks 812a. Generally, separators conventionally used in zinc/MnO₂ alkaline cells can be used for separator 890 in the present cell 810 having the anode 815 of the invention. Separator 890 can be of cellulosic film or a film formed of nonwoven material comprising polyvinylalcohol and rayon fibers. Separator 890 can be of a single layer of such nonwoven material or can be a composite having an outer layer of cellophane adhered to the nonwoven material. The nonwoven material can typically contain

between about 60 weight percent to 80 weight percent polyvinylalcohol fibers and between about 20 and 40 weight percent rayon fibers. Separator 890 can be positioned so that the cellophane layer is adjacent to either cathode 812 or anode 815. The above described separators are known and have been used in connection with conventional zinc/MnO₂ alkaline cell and are also suitable for use in the present alkaline cell 810. After the separator 890 is in place the solid porous zinc mass 815c (solid preform) of the invention can be inserted into the anode cavity 813. Alternatively, the solid porous zinc mass 815c can have a separator 890 wrapped around it and said solid porous mass with separator thereon, can then be inserted into the anode cavity 813. Alkaline electrolyte, preferably comprising potassium hydroxide, is then added to the anode cavity as above mentioned. The electrolyte is immediately absorbed by the solid porous zinc mass 815c whereupon the mass expands and forms a final fresh homogeneous anode 815 in the full shape of anode cavity 813. The final fresh anode 815 is typically of a soft, wet, spongy consistency.

After cell 810 is filled an insulating plug 860 is inserted into open end 816. Insulating plug 860 may be of polypropylene, talc filled polypropylene, sulfonated polyethylene or nylon. Plug 860 can have a thinned portion 865 therein typically of a small circular, oval or polygonal shape. Thinned portion 865 functions as a rupturable membrane which can be designed to rupture thereby releasing excessive gas within the cell. This guards against excessive buildup of gas pressure within the cell, for example, if the cell is subjected to excessive heat or abusive operating conditions. The plug 860 is preferably snap fitted around circumferential step 818 as shown in the Fig. 1 so that the plug locks in place into the open end 816. The peripheral edge 827 of casing 820 is crimped over the top of insulating plug 860. An insulating washer 880 is applied over the crimped peripheral edge 827 of casing 820. Insulating washer 880 can be a polyethylene coated paper washer. A terminal end cap 830 is welded to the head of current collector 840. An elongated current collector 840 is then inserted (force fitted) into aperture 844 of insulating plug 860 so that end cap 830 comes to rest against insulating washer 880. Current collector 840 can be selected from a variety of known electrically conductive metals found to be useful as current collector materials, for example, brass, tin plated brass, bronze, copper or indium plated brass. The current collector 840 used in the test cells was of brass. Conventional asphalt sealant may be preapplied around the current collector 840 before it is inserted into aperture 844. A film label 870 is applied around casing 820. The terminal end cap 830 becomes the negative

terminal of alkaline cell 810 and pip 825 at the closed end of casing 820 becomes the positive terminal.

The cell 810 shown in Figure 1 can be an AA cell. However, the alkaline cell shown in the figure is not intended to be restricted to any particular size. Thus, the method of the present invention is applicable to preparing anodes for AAAA, AAA, C and D size cylindrical alkaline cells as well as button shaped alkaline cells or prismatic cells or alkaline cells having an outer casing with one or more flat or curvilinear surfaces. The method of the invention can be applied to preparing zinc anodes for zinc/air cells, for example, zinc/air button cells which are commonly used for hearing aids.

Alkaline cell 810 is not intended to be restricted to any particular cathode chemistry, as long as the anode 815 is prepared by the method of the invention comprising a) forming a preformed dimensionally stabilized zinc mass, b) inserting the preformed mass into the cell's anode cavity 813, and c) adding aqueous electrolyte to the anode cavity to form a final fresh anode 815. The above cell (Fig. 1) can be an AAAA, AAA, AA, C or D cylindrical cells. These standard cell sizes are recognized in the art and are set by the American National standards Association or in Europe by the International Electrotechnical Commission (IEC). The AA cylindrical cell as referenced herein had standard overall dimensions as given by the American National Standards Institute (ANSI) battery specification ANSI C18.1M, Part 1-1999 as follows: The overall length from positive and negative terminal tips is between 49.2 mm and 50.5 mm and overall outside cell diameter is between 13.5 mm and 14.5 mm. The cell may also be in the form of flat or prismatic shaped cells.

The final fresh anode 815 preferably contains zero added mercury (less than 50 parts mercury per million parts total anode metal content (normally zinc), preferably less than 20 parts mercury per million parts total zinc in the anode). The cell 810 of the invention also preferably does not contain added amounts of lead and thus can be essentially lead free, that is, the total lead content is less than 30 ppm, desirably less than 15 ppm of zinc in the anode. The final fresh anode 815 desirably contains indium in amount between about 50 and 1000 ppm of the zinc, preferably between about 200 and 1000 ppm, desirably between about 200 and 500 ppm of the zinc.

A zinc/manganese dioxide alkaline cell, for example, can be fabricated in the form of a cylindrical cell 810 (Fig. 1) or button or coin cell 110 as shown (Fig. 2). The cylindrical cell 810 or button cell 110 may include conventional alkaline cell cathode mixture 812 or 170, respectively, comprising manganese dioxide. Such cathode mixtures,

can typically comprise for example MnO₂, 80 to 90 wt.%, graphite, for example, expanded graphite, between about 4 and 10 wt. %, and between about 5 and 10 wt.% of aqueous KOH electrolyte (aqueous KOH electrolyte is 30 to 40 wt.% KOH concentration, preferably between 35 and 40 wt.% KOH concentration). The aqueous KOH electrolyte preferably also contains about 2 wt.% ZnO. The cathode mixture can optionally also comprise between about 0.1 to 0.5 wt% of a polyethylene binder.

The final fresh anode composition 815 (Fig. 1) or 150 (Fig. 2) comprises: Zinc alloy powder 62 to 80 wt%, preferably between about 66 and 70 wt% (99.9 wt% zinc containing indium in total amount between about 200 and 1000 ppm zinc; typically between about 200 and 500 ppm zinc), an aqueous KOH solution comprising 38 wt% KOH and about 2 wt% ZnO; a polyvinyl alcohol binder (between about 0.15 and 1.0 wt.%, preferably between about 0.2 and 0.8 wt.%); a hydrogel binder comprising a cross-linked acrylic acid polymer gelling agent available commercially under the tradename "CARBOPOL C940" from B.F. Goodrich (e.g., 0.25 to 2 wt%) and preferably a starch graft copolymer such as a starch graft copolymer of polyacrylic acid and polyacrylamide commercially available commercially under the tradename "Waterlock A-221" from Grain Processing Co. (between 0.01 and 0.3 wt.%); dionyl phenol phosphate ester surfactant available commercially under the tradename "RM-510" from Rhone-Poulenc (between 0.025 and 0.15%). The zinc alloy, may typically contain between about 200 and 500 parts by weight indium per million parts zinc. Such zinc alloy have mean average particle size between about 30 and 1000 micron, desirably between about 30 and 400 micron, typically between about 100 and 400 micron. It will be understood that the particle size is based on the particles' long dimension in the case of irregularly shaped particles. The zinc particles may be spherical or predominantly spherical or alternatively may be predominantly of non spherical shape, for example, polygonal or acicular shape. It shall be understood that the term zinc as used herein shall include such zinc alloy powder, since the alloy powder is composed almost entirely of zinc and functions electrochemically as zinc.

Although the above binders, namely gelling agents CARBOPOL C940 and WATER-LOCK A-221 are preferred in conjunction with the polyvinylalcohol binder to form the anode mixture of the invention, other gelling agent binders may also be used in conjunction with the polyvinylalcohol. For example, the gelling agents for the zinc slurry can be selected from a variety of known gelling agents. Preferred gelling agents are substantially insoluble in the cell electrolyte so that the gelling agent does not migrate between the anode and cathode. The preferred gelling agents also do not lose water when the final anode of the invention is left in storage. Suitable gelling agents which may be

used as binders in conjunction with the polyvinylalcohol binder for the anode mixture of the invention, for example, may be carboxymethyl cellulose or crosslinked carboxymethyl cellulose, methyl cellulose, crosslinked polyacrylamides, crosslinked acrylic acid polymers such as CARBOPOL C-940 from B.F. Goodrich Co., starch graft copolymers such as WATER-LOCK A-221 starch-graft copolymer of polyacrylic acid and polyacrylamide from Grain Processing Co., and alkali hydrolyzed polyacrylonitrile such as WATER-LOCK A 400 from Grain Processing Co. Although any of these gelling agents can be employed alone or in combination, at least one of the gelling agents may advantageously be selected from crosslinked acrylic acid polymer such as CARBOPOL C940 or SIGMA POLYGEL 4P gelling agents or a starch graft copolymer such as WATER-LOCK A-221 copolymer. Additionally the polyvinylalcohol, preferably of M.W. between about 85000 and 146000 is added as described in the above to form the wet anode mixture of the invention which can be dried and converted into a dry solid porous mass (dry solid premold) of the invention which in turn can be inserted into the anode cavity of an alkaline cell. Aqueous alkaline electrolyte, preferably comprising potassium hydroxide is then added to the solid porous zinc mass whereupon the electrolyte is absorbed in the solid mass causing the mass to expand and convert into the final anode. The polyvinylalcohol binder as well as the acrylic acid polymer CARBOPOL C940 binder are chemically very stable in alkaline electrolyte and are desirable binders particularly when employed in combination for the anode of the present invention. The polyvinylalcohol in particular provides added structural integrity and holds the zinc particles together in a tight network so that a free standing solid porous mass (solid preform) may be formed.

In accordance with the invention a wet zinc paste 815a is first prepared and molded to form a wet preform mass 815b in the near shape of the anode cavity. This can be done conveniently by pouring or extruding the wet paste 815a into die cavity 630 of steel or plastic die 600 as shown in Fig. 3A. Die 600 has a body portion 610 with cavity 630 running therethrough. The die body sits on detachable base 620 (Fig. 3A). Die cavity 630 is in the approximate shape of the cell's anode cavity. The wet zinc paste 815a is molded under pressure by applying a pressure to the plunger top 640 thereby injecting plunger 645 into die cavity 630, for example, in 2-3 seconds, causing the wet zinc paste 815a to become compacted and molded into the cavity 630 shape. Typically, a moderate force can be applied to the plunger, desirably under about 400 pounds force, typically between about 10 and 300 pounds. Such force is applied in this manner to the exposed surface of the wet zinc paste 815a by a stroke of plunger 645, for die cavities 630 having diameter, for example, between about 3 and 7 mm. The amount of force is adjusted depending on the diameter or

width of the die cavity 630 and the amount of the wet zinc paste present within the die. Smaller diameter cavities and smaller amount of the wet zinc paste require less plunger force than larger diameter cavities and larger amount of the wet zinc paste. Die base 620 is then detached from the die body 610. The molded wet zinc mass (wet preform) 815b can be pushed through the die cavity 630 by a second stroke of plunger 645 (shown in retracted position in Fig. 3B). The wet preform 815b (Fig. 3B) emanating from die cavity 630 (Fig. 3B) is dimensionally stable, that is, has sufficiently strong structural integrity so that it can stand alone outside of the die while retaining at least its general molded shape.

Thus, the wet zinc mass 815b (wet preform) in a preferred embodiment can be placed on a flat tray or surface 720 which can be inserted in an oven 700 (Fig. 3C). Optionally, separator 890 can be wrapped around wet zinc mass 815b so that wet zinc mass 815b with separator 890 thereon is placed in an oven 700. In such case separator 890 can be wrapped around wet zinc mass 815b so that it covers at least the bottom and side surfaces of said wet mass 815b in a configuration shown, for example, in Fig. 1. This may be accomplished by wrapping a single sheet of separator 890 around the surfaces of wet zinc mass 815b. Alternatively, separator 890 may be applied in strips, for example two strips, oriented at right angles to each other and overlapping at their mid sections. Such overlapping strips can be placed under the wet zinc mass 815b and the strips folded up to cover at least the side and bottom surfaces of said wet zinc mass 815b, resulting in the configuration, for example, shown in Fig. 1. Separator 890 may be of electrolyte permeable material conventionally employed in alkaline cells. The separator 890 may adhere to the wet zinc mass 815b. Having the separator 890 wrapped around the wet zinc mass 815b avoids the need of inserting the separator 890 into the anode cavity before anode material is inserted therein.

The wet zinc mass 815b (wet preform), with or without separator 890 wrapped around it, is then heated in an oven 700 at elevated temperature, desirably between about 55°C and 120°C, typically at about 55°C in ambient air (or inert gas). Oven 700 can be a conventional oven heated by an electric or gas source 710. Such heating evaporates at least a portion of the free water therein, thereby resulting in a dried and porous zinc mass (solid preform) 815c. If the wet zinc mass 815b was wrapped with separator 890, then the solid zinc mass 815c will also have the separator 890 intact around said solid zinc mass 815b and typically adhering thereto. The dry zinc mass 815c (Fig. 3D) is dimensionally stable and thus can stand alone without change in at least its general shape. It can be stored in sealed containers until time for cell assembly. The zinc mass 815c (solid preform), with or without separator 890 wrapped around it, is then inserted into the

cell's anode cavity 813 and aqueous electrolyte added thereby expanding the zinc mass to form the final fresh anode 815.

The wet zinc paste 815a inserted into die cavity 630 is formed as follows: A mixture of zinc particles, surfactant, hydrogel binders, polyvinylalcohol binder and water is blended into a paste using an electric/mechanical blender for a period of time, typically about 2-3 minutes, until the paste has a homogeneous consistency. The amount of binders and water in the blend are adjusted to control the paste consistency. The wet paste is then inserted into a steel, ceramic or plastic die having a die cavity 630 (Fig. 3A) in the approximate shape of the anode cavity, but preferably slightly smaller. For example, the diameter of die cavity 630 may typically be between about 10 and 40 percent smaller than the inside diameter of anode cavity 813. The wet paste assumes the shape of the die under pressure in about 2-3 seconds. The wet paste is then removed in its entirety from the die and is now in the form of a wet zinc mass (wet preform) in the near shape of the anode cavity. The binders in the wet mass, particularly the polyvinylalcohol, impart sufficient structural integrity to the mass so that the molded wet preform can stand alone outside of the die.

The wet paste forming the wet zinc mass 815b (wet preform) comprises a mixture of zinc particles, surfactant, hydrogel binders, polyvinylalcohol binder and water. The wet paste is formed without adding aqueous electrolyte. The surfactant is preferably a dinonyl phenol phosphate ester surfactant such as that available commercially under the tradename "RM-510" from Rhone-Poulenc. The binders comprises a) one or more hydrogel binders (gelling agents) and b) a polyvinylalcohol binder. A preferred hydrogel binder is a cross-linked acrylic acid polymer gelling agent available commercially under the tradename "CARBOPOL C940" from B.F. Goodrich. The CARBOPOL C940 binder may be employed alone. Preferably, however, a hydrolyzed polyacrylonitrile grafted onto a starch backbone commercially available commercially under the tradename "Waterlock A-221" from Grain Processing Co is added to form the total hydrogel binder. The hydrogel binders function more as binders in the wet preform, since the wet preform does not include alkaline electrolyte. (The hydrogel become gelling agents in the presence of alkaline electrolyte.)

The wet preform 815b may have the following composition: zinc (80 to 94 wt.%), surfactant, e.g. dinonyl phenol phosphate ester RM-510 surfactant (0.05 to 0.2 wt.%); total binders (0.5 to 3 wt.%) comprising for example, CARBOPOL C940 binder (0.5 to 3 wt.%) and WATERLOCK A-221 binder (0.05 to 0.33 wt.%) and polyvinylalcohol (0.2 to 1 wt.%); and water (3 to 18 wt.%).

The wet preform 815b is heated in an oven at temperature desirably between about 55°C and 120°C, preferably at about 55°C, for a period of about 2 to 3 hours or less in ambient air (or inert gas). Such heating evaporates at least a portion of the water in the wet preform thereby forming a solid, porous zinc mass (solid preform) 815C in the near shape of the anode cavity. It is desirable to keep the heating temperature below about 120°C to avoid degradation of the polyvinylalcohol and/or gelling agents within the wet preform 815b. The solid preform 815C may desirably have the following composition: zinc (96 to 99 wt. %); surfactant, e.g. dionyl phenol phosphate ester RM-510 surfactant (0.06 to 0.25 wt.%); total binders (0.5 to 3.3 wt.%) comprising for example, CARBOPOL C940 binder (0.5 to 3.3 wt.%) and WATERLOCK A-221 binder (0.05 to 0.37 wt.%) and polyvinylalcohol (0.22 to 1.2 wt.%). The mean average zinc particle size may be between about 30 and 1000 micron, typically between about 100 and 400 micron. The solid porous zinc mass (solid preform) may be stored for very long periods, essentially for many months or even years, since there is no component therein which will react with each other or with the zinc particles. The solid preform may be stored in air under ambient conditions, since exposure to air does not cause noticeable deterioration of the zinc particles or other components within the dry preform. The solid porous zinc mass (solid preform) 815C is characterized by pockets of microscopic void spaces which appear between the individual zinc particles resulting in a porosity of the solid preform of between about 25 and 50 percent, typically between about 40 and 50 percent. Such microscopic void spaces between zinc particles are clearly seen in the scanning electron micrograph of the solid porous zinc mass 815C shown in Fig. 4. These void spaces were formerly filled by the water which was evaporated from the mass. The binder material such as polyvinylalcohol is shown in Fig. 4 between the zinc particles and holds the zinc particles together in a solid porous mass. Surprisingly, the polyvinylalcohol, preferably at molecular weight between about 85000 and 146000, functions as a glue to hold the zinc particles together in the solid porous zinc mass (solid preform). The polyvinylalcohol imparts structural integrity to prevent collapse of the solid preform after formation as well as during storage. The solid preform can be placed in storage for long periods, for example, many months or even years before it is desired to insert it into the cell's anode cavity.

When it is desired to load the alkaline cell with anode material, the solid porous zinc mass 815b (solid preform), with or without separator 890 wrapped around it, is inserted in the cell's anode cavity. Alkaline electrolyte, preferably an aqueous solution of potassium hydroxide, is then added to the anode cavity. Desirably the aqueous alkaline electrolyte comprising potassium hydroxide (concentration between about 35 and 40 wt.%)

KOH, 2 wt. % ZnO) is added to the anode cavity in amount so that the weight ratio of aqueous electrolyte to the solid porous zinc mass (solid preform) is between about 0.25 and 0.75. The aqueous alkaline electrolyte becomes absorbed into the solid preform causing the preform to expand and tightly fill the anode cavity. The addition of the aqueous alkaline electrolyte also activates the gelling characteristics of the hydrogel binders. The zinc particles become held together in a tighter network than in conventional zinc slurry anodes and there are no visible air pockets within the final anode when the anode is viewed in normal size by X-ray photography. The tighter network of zinc particles tends to improve conductivity and overall performance of the anode. The polyvinylalcohol functions as a glue which binds the zinc particles together, whereas the hydrogel binders serve mainly as a gelling agents, that is, they absorb aqueous electrolyte solution and also cause expansion of the dry zinc mass when the electrolyte is added thereto.

In the button cell 110 shown in Fig.2, a disk-shaped cylindrical housing 130 is formed having an open end 132 and a closed end 138. Housing 130 is formed from nickel-plated steel. An electrical insulating member 140, preferably a cylindrical member having a hollow core, is inserted into housing 130 so that the outside surface of insulating member 140 abuts and lines the inside surface of housing 130. Optionally, the inside surface of housing 130 can be coated with a polymeric material, or asphalt sealant and the like, that interfaces between insulator 140 and the inside surface housing 130. Insulator 140 can be formed from a variety of thermally stable insulating materials which resist attack by alkaline electrolyte, for example, nylon or polypropylene.

With reference to the button cell of Fig. 2, the cathode mixture 170 comprising MnO_2 (EMD), graphite, aqueous electrolyte can be prepared by simple mixing at ambient temperature in a conventional blender until a homogenous mixture is obtained. The graphite can be flaky natural crystalline graphite, flaky crystalline synthetic graphite, expanded graphite or any mixture thereof. The cathode composition may be as described above with reference to the cylindrical cell 810 (Fig. 1). The cathode 170 is applied as a layer or a pressed disk abutting the inside surface of the closed end 138 of housing 130. The separator sheet 160 is placed overlying cathode 170. The separator 160 can be a conventional ion porous separator as described above with respect to separator 890 (Fig.1). In the specific embodiment shown in Fig. 2 the separator 160 may comprise an outer layer of cellulose or cellophane (abutting anode 150) and an inner layer of a nonwoven material composed of cellulosic (rayon) and polyvinylalcohol fibers.

The anode 150 can be prepared in accordance with the method of the invention as above described in which a wet zinc mass (wet preform) is prepared and molded into the near shape of the disk shaped anode cavity 153 (Fig. 2). The wet zinc mass (wet preform) is then dried to form a solid porous zinc mass (solid preform). The solid preform is then inserted into anode cavity over separator 160. Aqueous alkaline electrolyte is then added to the anode cavity 153 and absorbed by the solid preform to form the final fresh anode 150. The anode cover 120, formed preferably of nickel-plated steel is inserted into the open end 132 of housing 130. An anode current collector 115 comprising a sheet of brass, tin-plated brass, bronze, copper or indium-plated brass can optionally be welded to the inside surface of anode cover 120. Peripheral edge 135 of housing 130 is crimped over the exposed insulator edge 142 of insulating member 140. The peripheral edge 135 bites into insulator edge 142 closing housing 130 and tightly sealing the cell contents therein. The anode cover 120 also functions as the negative terminal of the cell and the housing 130 at the closed end 138 functions as the cell's positive terminal.

A comparative AA cylindrical cell 810 was prepared employing conventional MnO_2 cathode, separator and anode made in conventional manner using a zinc slurry. A set of test AA cells were prepared with the same cathode composition, separator, but the anode was made by the method of the invention. The comparative AA cell 810 was prepared with conventional anode and cathode and separator. The anode was prepared from a conventional zinc slurry mixture which was pumped into the anode cavity 813. Test cylindrical AA cells 810 were then prepared. The cathode and separator of the test cells were the same as that used in the comparative cell. The separator 890 was a conventional ion porous separator consisting of an inner layer of a nonwoven material of cellulosic (rayon) and polyvinylalcohol fibers and an outer layer of cellophane. However, the anode 815 in the test cells was prepared in accordance with the method of the invention in which a wet zinc mass (wet preform) was molded into the near shape of the anode cavity. The wet preform was then dried to form a solid porous zinc mass (solid preform) as above described. The solid preform was inserted into anode cavity 813. Aqueous alkaline electrolyte was added to the anode cavity and absorbed by the solid preform to form the final anode. The comparative AA cell and test AA cells each had the same amount of zinc, namely, 4.6 grams. The cells were balanced so that the theoretical milliamp-hrs capacity of MnO_2 (based on 370 milliamp-hours per gram MnO_2) divided by the theoretical capacity of zinc (based on 820 milliamp-hours per gram zinc) is about 1. The performance of the cells, service life (milliamp-hrs) and energy output (milliwatt-

hrs) was determined by discharging at constant current drains of 50 milliAmp and 500 milliAmp to cut off voltage of 0.5 volts.

EXAMPLE 1

(Comparative Test – Conventional Anode Slurry/

Conventional MnO₂ Cathode)

Test cylindrical AA cells of the general configuration shown in 810 (Fig. 1) were prepared. The cathode 812 in the comparative AA cell and test AA cells, for example, may have the following representative compositions: 80-90 wt% of electrolytic manganese dioxide (e.g., Trona D from Kerr-McGee), 4-10 wt% of expanded graphite (Timcal E-BNB90, BET surface of 24.3 m²/g), 5-10 wt% of an aqueous KOH solution having a KOH concentration of about 35-40 wt.%. A specific cathode composition for the comparative AA cell and test AA cells used for the performance tests reported in the Tables was as follows:

		Cathode Composition ¹
		<u>Wt. %</u>
15	MnO ₂ (EMD)	87
	Expanded graphite (Timcal E-BNB90)	8
	KOH aqueous Solution (36 wt% 20 KOH and 2 wt% ZnO)	<u>5</u>
		100

Notes:

1. Conversion to volume percent can be made using the following real densities: MnO₂ (EMD), 4.48 g/cc; expanded graphite (Timcal E-BNB90), 2.25 g/cc; and 36 wt% KOH aqueous solution, 1.35 g/cc.

The anode of the comparative test cell 810 was prepared in conventional manner by preparing a zinc anode slurry as described above in the Background Section. Before the anode slurry was added into the anode cavity, ~1.25 g of an aqueous KOH solution comprising 38 wt% KOH and about 2 wt% ZnO was added into the cell casing to fill the pores within the MnO₂ cathode. Subsequently, the anode slurry was pumped into the anode cavity using a conventional slurry pump, normally employed in the service of pumping anode slurries. Although care was taken to prevent air from entering the slurry mixture there were nevertheless several visible air pockets within the final anode slurry as introduced into the anode cavity. Such air pockets were visible to the

naked eye from X-ray photographs of the cell taken without magnification. The zinc slurry which filled the anode cavity 813 formed anode 815 having 4.6 grams zinc. The final anode 815 had the following composition: 70 wt% of Zinc alloy powder (99.9 wt% zinc containing indium in total amount of 500 ppm zinc, 29.4 wt% of an aqueous KOH solution comprising 38 wt% KOH and about 2 wt% ZnO; 0.44 wt% of a cross-linked acrylic acid polymer gelling agent available commercially under the trade name "CARBOPOL C940" from B.F. Goodrich and 0.032 wt% of a hydrolyzed polyacrylonitrile grafted onto a starch backbone commercially available commercially under the tradename "Waterlock A-221" from Grain Processing Co.; 0.117 wt% of dinonyl phenol phosphate ester surfactant available commercially under the tradename "RM-510" from Rhone-Poulenc. The zinc alloy mean average particle size was about 320 micron. The separator 890 was a conventional dual layered cellulosic separator employing an outer layer comprising rayon and polyvinylalcohol (facing cathode 812) and inner layer of cellophane facing anode 815.

Fresh AA cells of Example 1 were discharged at a constant rate of 50 milliAmp. In separate tests batches of fresh AA cells 810 of Example 1 were discharged at a constant rate of 500 milliAmp.

At discharge of 50 milliAmp, the capacity obtained at a cut off voltage of 0.5 Volts was 3010 milliAmp-hrs. The average voltage at 50% capacity was 1.22 Volt. The energy output of the cell at 0.5V cutoff was 3520 milliWatt-hrs.

At discharge of 500 milliAmp, the capacity obtained at a cut off voltage of 0.5 Volts was 1550 milliAmp-hrs. The average voltage at 50% capacity was 1.06 Volt. The energy output of the cell at 0.5V cutoff was 1590 milliWatt-hrs.

A cell gassing test was conducted by measuring the amount of gas generated from the zinc anode when the fresh zinc anode was placed in a sealed bag and stored at 60°C for 4 weeks. The amount of gassing was 0.0120 ml gas per gram of anode.

EXAMPLE 2

(Anode from Solid Porous Zinc Mass/

Conventional MnO₂ Cathode)

Test AA size cells 810 were prepared as in Example 1 except that the anode 815 was formed from the wet zinc mass (wet preform) which was molded into the approximate shape of the anode cavity 813 and then dried to produce the solid porous zinc mass (solid preform) 815C of the invention. The solid preform was inserted into the anode cavity 813 and then aqueous potassium hydroxide electrolyte (concentration between about 35 and 40 wt.% KOH and 2 wt.% ZnO) was added. The solid porous zinc

mass (solid preform) immediately absorbed the alkaline electrolyte and expanded to form the final fresh wet anode as described in the description hereinabove. The cathode composition comprising MnO_2 was the same as used in Example 1. The cell had 4.6 grams of zinc as in Example 1 and was balanced so that the theoretical capacity of the zinc divided by the theoretical capacity of the MnO_2 was about 1.

The wet zinc mass (wet preform) had the following composition:

	Wet Preform, Wt. %
Zinc	89.20
Surfactant	
Dinonyl phenol phosphate	
ester surfactant (RM-510)	0.101
Binders	
CARBOPOL C940 binder	0.978
WATERLOCK A-221 binder	0.101
Polyvinylalcohol	0.305
(M.W. 85000 to 146000)	
Water	<u>9.32</u>
	100.00

The wet zinc mass is molded into the near shape, though somewhat smaller size of the anode cavity. The molded wet zinc mass (wet preform) is then dried by heating in an oven at about 55°C for a period of about 2 to 3 hours to evaporate water leaving a solid porous zinc mass (solid preform) having a porosity between about 40 and 50%. The solid porous zinc mass (solid preform) has the following composition:

	Solid Porous Zinc
	<u>Mass (Solid Preform)</u>
	<u>Wt. %</u>
Zinc	98.4
Surfactant	
Dinonyl phenol phosphate	
ester surfactant (RM-510)	0.112
Binders	
CARBOPOL C940 binder	1.08
WATERLOCK A-221 binder	0.112
Polyvinylalcohol	<u>0.336</u>
	100.00

After the solid porous zinc mass (solid preform) is inserted into the anode cavity an aqueous potassium hydroxide electrolyte comprising 38 wt% KOH and about 2 wt% ZnO was added in amount approximately about 0.7 part by weight aqueous electrolyte to 1 part by weight solid preform. The solid preform immediately absorbed the aqueous electrolyte and expanded to fill the anode cavity to form the final fresh anode. The final fresh anode did not have any discernible air pockets therein when the anode was viewed with the aid of X-ray photographs of the cell taken without magnification. The polyvinylalcohol within the final fresh anode helped to hold individual zinc particles in close proximity to one another within a tight network.

Fresh AA cells of Example 2 were discharged at a constant rate of 50 milliAmp. In separate tests batches of fresh AA cells of Example 2 were discharged at a constant rate of 500 milliAmp.

At discharge of 50 milliAmp, the capacity obtained at a cut off voltage of 0.5 Volts was 2930 milliAmp-hrs. The average voltage at 50% capacity was 1.23 Volt. The energy output of the cell at 0.5V cutoff was 3450 milliWatt-hrs.

At discharge of 500 milliAmp, the capacity obtained at a cut off voltage of 0.5 Volts was 1530 milliAmp-hrs. The average voltage at 50% capacity was 1.07 Volt. The energy output of the cell at 0.5V cutoff was 1630 milliWatt-hrs.

A cell gassing test was conducted by measuring the amount of gas generated from the zinc anode when the fresh zinc anode was placed in a sealed bag and stored at 60°C for 4 weeks. The amount of gassing was 0.0122 ml gas per gram of anode.

EXAMPLE 3

(Anode from Solid Porous Zinc Mass/
Conventional MnO₂ Cathode)

Test AA size cells 810 were prepared as in Example 1 except that the anode 815 was formed from the wet zinc mass (wet preform) which was molded into the approximate shape of the anode cavity 813 and then dried to produce the solid porous zinc mass (solid preform) 815C of the invention. The solid preform was inserted into the anode cavity 813 and then aqueous potassium hydroxide electrolyte (concentration between about 35 and 40 wt.% KOH and 2 wt.% ZnO) was added. The solid porous zinc mass (solid preform) immediately absorbed the alkaline electrolyte and expanded to form the final wet anode as described in the description hereinabove. The cathode composition comprising MnO₂ was the same as used in Example 1. The cell had 4.6 grams of zinc as in Example 1 and was balanced so that the theoretical capacity of the zinc divided by the theoretical capacity of the MnO₂ was about 1.

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The wet zinc mass (wet preform) had the following composition which involved a lower zinc composition than in Example 2:

	<u>Wet Preform, Wt.%</u>
Zinc	86.65
Surfactant	
Dinonyl phenol phosphate ester surfactant (RM-510)	0.106
Binders	
CARBOPOL C940 binder	1.27
WATERLOCK A-221 binder	0.106
Polyvinylalcohol (M.W. 85000 to 146000)	0.633
Water	<u>11.17</u>
	100.00

The wet zinc mass is molded into the near shape, though somewhat smaller size of the anode cavity. The molded wet zinc mass (wet preform) is then dried by heating in an oven at about 55°C for a period of about 2 to 3 hours to evaporate water leaving a solid porous zinc mass (solid preform) having a porosity between about 40 to 50%. The solid porous zinc mass (solid preform) has the following composition:

	<u>Solid Porous Zinc Mass (Solid Preform)</u>
	<u>Wt.%</u>
Zinc	97.55
Surfactant	
Dinonyl phenol phosphate ester surfactant (RM-510)	0.119
Binders	
CARBOPOL C940 binder	1.43
WATERLOCK A-221 binder	0.119
Polyvinylalcohol	<u>0.713</u>
	100.00

After the solid porous zinc mass (solid preform) is inserted into the anode cavity an aqueous potassium hydroxide electrolyte comprising 38 wt% KOH and about 2 wt% ZnO was added in amount approximately about 0.7 part by weight aqueous electrolyte to 1 part by weight solid preform. The solid preform immediately absorbed

the aqueous electrolyte and expanded to fill the anode cavity to form the final fresh anode. The final fresh anode did not have any discernible air pockets therein when the anode was viewed with the aid of X-ray photographs of the cell taken without magnification. The polyvinylalcohol within the final fresh anode helped to hold individual zinc particles in close proximity to one another within a tight network.

Fresh AA cells of Example 3 were discharged at a constant rate of 500 milliAmp.

At discharge of 500 milliAmp, the capacity obtained at a cut off voltage of 0.5 Volts was 1400 milliAmp-hrs. The average voltage at 50% capacity was 1.06 Volt. The energy output of the cell at 0.5V cutoff was 1470 milliWatt-hrs.

The test results are summarized in the following Tables:

TABLE 1

Performance Comparison Of AA Size Zinc/MnO₂ Alkaline Cells,
Discharged at 50 mAmp to Cut Off Voltage of 0.5V

	Capacity, mAmp-hrs.	Average Voltage to 50% Capacity	Energy Output, mWatt-Hrs.	Anode Gassing ¹ , ml. gas per gram anode
Comparative Cell (Anode Zinc Slurry, Example 1)	3010	1.22	3520	0.0120
Test Cell (Molded Zinc Anode, Example 2)	2930	1.23	3450	0.0122
Test Cell (Molded Zinc Anode, Example 3)	-	-	-	-

Notes:

1. The anode gassing was conducted by measuring the amount of gas generated from the zinc anode when the fresh zinc anode was placed in a sealed bag and stored at 60°C for 4 weeks.

TABLE 2

Performance Comparison Of AA Size Zinc/MnO₂ Alkaline Cells,
Discharged at 500 mAmp to Cut Off Voltage of 0.5V

	Capacity, mAmp-hrs.	Average Voltage to 50% Capacity	Energy Output, mWatt-Hrs.	Anode Gassing ¹ , ml. gas per gram anode
Comparative Cell (Anode Zinc Slurry, Example 1)	1550	1.06	1590	0.0120
Test Cell (Molded Zinc Anode, Example 2)	1530	1.07	1630	0.0122
Test Cell (Molded Zinc Anode, Example 3)	1400	1.06	1470	-

Notes:

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1. The anode gassing was conducted by measuring the amount of gas generated from the zinc anode when the fresh zinc anode was placed in a sealed bag and stored at 60°C for 4 weeks.

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As shown from the data reported in the above tables, the overall performance of the AA zinc/MnO₂ cells employing the molded zinc anode made by the process of the invention were generally comparable to the same cells employing conventional zinc anode slurry. Gassing tests of fresh molded zinc anode made by the method of invention were also comparable to zinc anode made by conventional anode slurry.

C L A I M S

1. A method of forming an anode for an alkaline cell comprising the step of:
 - a) forming a mixture comprising zinc particles, a first fluid, and a binder comprising a gluing agent for binding zinc particles; and
 - b) at least partially drying the mixture thereby producing a dimensionally stabilized mass comprising said zinc particles.
2. The method of claim 1, comprising the additional steps of:
 - c) inserting said dimensionally stabilized mass into an alkaline cell; and
 - d) adding a second fluid to said mass in said cell whereby the second fluid is absorbed into said mass to form the anode.
3. The method of claim 1, wherein said first fluid comprises water.
4. The method of claim 2, wherein said second fluid comprises aqueous alkaline electrolyte.
5. The method of claim 1, wherein said gluing agent for binding the zinc particles comprises polyvinylalcohol.
6. The method of claim 1, wherein said dimensionally stabilized mass is a solid porous mass comprising zinc particles.
7. The method of claim 1, wherein said mixture is at least substantially wrapped with a separator material prior to at least partially drying said mixture.
8. The method of claim 1, wherein said mixture is molded into a dimensionally stabilized shape prior to at least partially drying said mixture.
9. The method of claim 5, wherein the solid porous mass is inserted into the anode cavity of an alkaline cell before adding said second fluid in step (d).
10. The method of claim 9, wherein said solid porous mass expands as said second fluid is absorbed therein.
11. The method of claim 4, wherein the aqueous alkaline electrolyte comprises potassium hydroxide.
12. The method of claim 1, wherein said dimensionally stable mass is storable in ambient air.
13. The method of claim 5, wherein the polyvinylalcohol has a molecular weight between about 85000 and 146000.
14. The method of claim 1, wherein said drying in step b) is effected by heating said mixture.

15. The method of claim 1, wherein said binder further comprises a crosslinked acrylic acid polymer gelling agent.

16. The method of claim 1, wherein said binder further comprises a gelling agent comprising a starch graft copolymer of polyacrylic acid and polyacrylamide.

5 17. The method of claim 1, wherein said binder further comprises CARBOPOL C940 crosslinked acrylic acid polymer.

18. The method of claim 1, wherein said binder further comprises a mixture of CARBOPOL C940 crosslinked acrylic acid polymer and WATER-LOCK A-221 starch graft copolymer.

0 19. The method of claim 1, wherein said mixture further comprises indium in total amount between about 200 and 1000 ppm of the zinc.

20. The method of claim 1, wherein said mixture further comprises a surfactant.

5 21. The method of claim 20, wherein said surfactant comprises an organic phosphate ester.

22. The method of claim 8, wherein said mixture is molded into the approximate shape of the anode cavity of an alkaline cell.

23. A method of forming an anode for an alkaline cell comprising the step of:

20 a) forming a mixture comprising zinc particles, a binder comprising an alcohol such as polyvinylalcohol, and water;

b) drying the mixture to evaporate at least a portion of the water therein and thereby producing a dimensionally stabilized mass comprising said zinc particles;

25 c) inserting said dimensionally stabilized mass into the anode cavity of an alkaline cell; and

d) adding a fluid to the anode cavity whereby said fluid is absorbed by said mass and thereby forms said anode.

24. The method of claim 23, wherein said fluid comprises aqueous alkaline electrolyte.

30 25. The method of claim 23, wherein said dimensionally stabilized mass is a solid porous mass comprising zinc particles.

26. The method of claim 25, wherein said solid porous mass expands as said fluid is absorbed therein in step (d).

35 27. The method of claim 23, wherein said mixture is at least substantially wrapped with a separator material prior to drying said mixture.

28. The method of claim 23, wherein said mixture is molded into a designated shape prior to drying said mixture.

29. The method of claim 24, wherein the aqueous alkaline electrolyte comprises potassium hydroxide.

5 30. The method of claim 23, wherein said drying in step b) is effected by heating said mixture.

31. The method of claim 23, wherein the polyvinylalcohol has a molecular weight between about 85000 and 146000.

10 32. The method of claim 23, wherein said binder further comprises a gelling agent.

33. The method of claim 23, wherein said binder further comprises a crosslinked acrylic acid polymer gelling agent.

34. The method of claim 23, wherein said binder further comprises a gelling agent comprising a starch graft copolymer of polyacrylic acid and polyacrylamide.

15 35. The method of claim 23, wherein said binder further comprises CARBOPOL C940 crosslinked acrylic acid polymer.

36. The method of claim 23, wherein said binder further comprises a mixture of CARBOPOL C940 crosslinked acrylic acid polymer and WATER-LOCK A-221 starch graft copolymer.

20 37. The method of claim 23, wherein said mixture prior to drying further comprises indium in total amount between about 200 and 1000 ppm of the zinc.

38. The method of claim 23, wherein said mixture prior to drying further comprises a surfactant.

25 39. The method of claim 38, wherein said surfactant comprises an organic phosphate ester.

40. The method of claim 25, wherein said solid porous mass is storable in ambient air.

41. The method of claim 23, wherein said mixture is molded into the approximate shape of the anode cavity of an alkaline cell prior to drying said mixture.

30 42. An electrochemical cell comprising a housing, a positive and a negative terminal, an anode comprising zinc and polyvinylalcohol, an aqueous alkaline electrolyte solution, a separator, and a cathode comprising a cathode active material.

43. The cell of claim 42, wherein said cell is a primary cell.

35 44. The cell of claim 42, wherein the aqueous electrolyte comprises potassium hydroxide.

45. The cell of claim 42, wherein the polyvinylalcohol has a molecular weight between about 85000 and 146000.

46. The cell of claim 42, wherein the cathode comprises manganese dioxide.

47. The cell of claim 42 wherein the zinc comprises zinc particles having a mean average particle size between about 30 and 1000 micron.

48. The cell of claim 42, wherein the zinc comprises zinc particles having a mean average particle size between about 30 and 400 micron.

49. The cell of claim 42, wherein said anode further comprises a binder comprising a gelling agent comprising a crosslinked acrylic acid polymer.

50. The cell of claim 42, wherein said anode further comprises a binder comprising a gelling agent comprising starch graft copolymer of polyacrylic acid and polyacrylamide.

51. The cell of claim 42, wherein said anode further comprises a surfactant.

52. The cell of claim 51, wherein said surfactant comprises an organic phosphate ester.

53. The combination of an alkaline cell housing having an anode cavity therein and a porous mass inserted into said anode cavity, said mass comprising zinc particles bound together forming a network of zinc particles with void spaces therebetween, said mass being dimensionally stabilized.

54. The combination of claim 53, wherein said mass is a solid porous mass.

55. The combination of claim 54, wherein said solid porous mass is at least substantially dry.

56. The combination of claim 53, wherein said mass is at least substantially wrapped with a separator material.

57. The combination of claim 56, wherein said separator material adheres to said solid mass.

58. The combination of claim 54, wherein said solid porous mass at least substantially fills said anode cavity.

59. The combination of claim 53, wherein said network of bound zinc particles extends at least substantially throughout said mass.

60. The combination of claim 59, wherein said zinc particles is uniformly distributed within said network.

61. The combination of claim 54, wherein said mass has a porosity of between about 25 and 50 percent by volume.

62. The combination of claim 51, wherein polyvinylalcohol coats a portion of the surface of said zinc particles thereby binding said zinc particles together forming said network of zinc particles.

63. The combination of claim 62, wherein said polyvinylalcohol has a molecular weight between about 85000 and 146000.

64. The combination of claim 53, further comprising a binder comprising acrylic acid polymer between said zinc particles.

65. The combination of claim 53, further comprising a surfactant.

66. The combination of claim 65, wherein said surfactant comprises an organic phosphate ester.

67. The combination of claim 53, wherein said zinc particles have a mean average size of between about 30 and 1000 micron.

68. The combination of claim 53, wherein said zinc particles have a mean average size of between about 30 and 400 micron.

69. The combination of claim 53, wherein said mass further comprises indium in total amount between about 200 and 1000 parts by weight indium per million parts zinc.

70. The combination of an alkaline cell housing having an anode cavity therein and a dimensionally stabilized mass comprising anode active material inserted into said anode cavity.

71. The combination of claim 70, wherein said mass at least substantially fills said anode cavity.

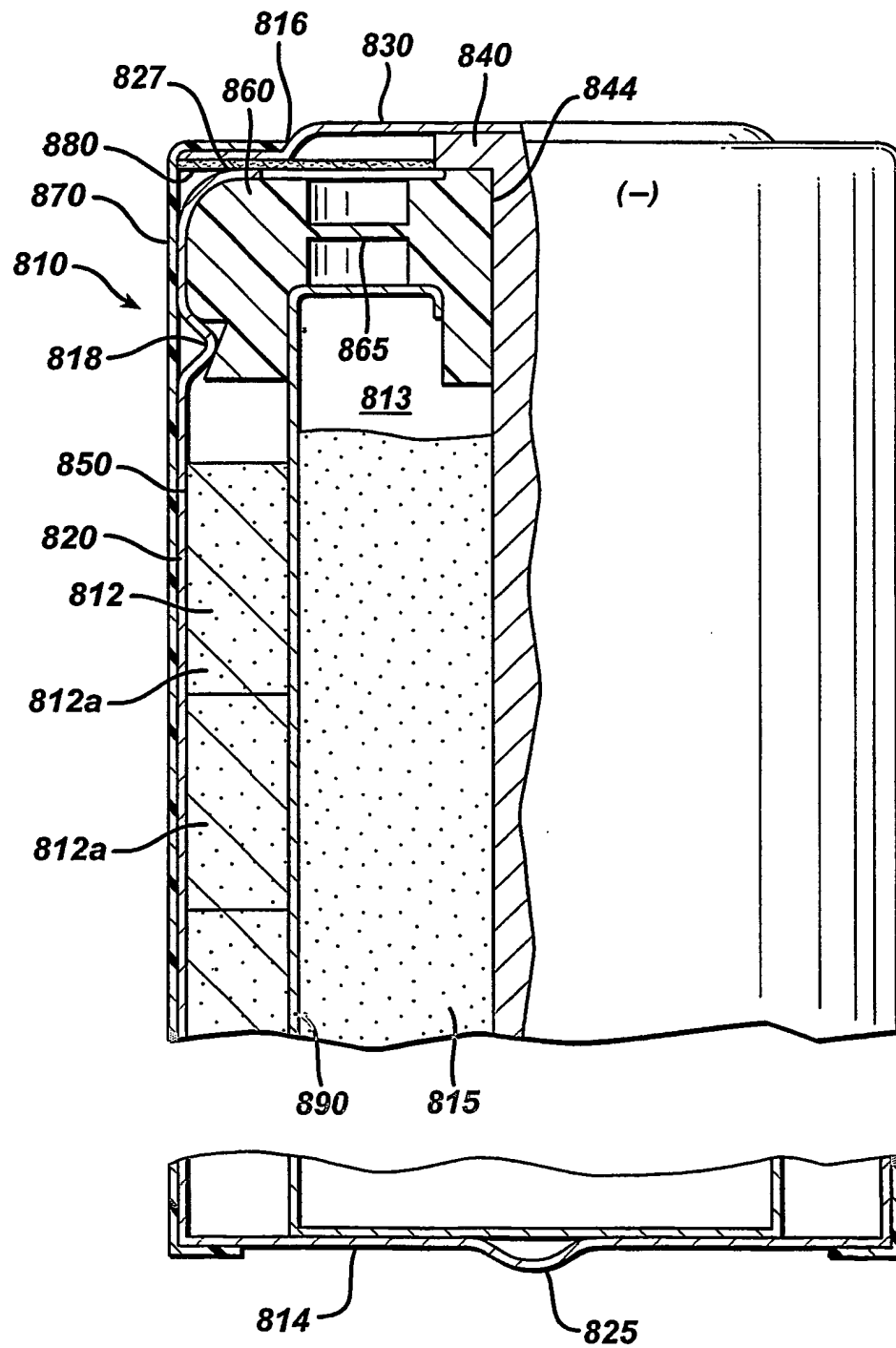
72. The combination of claim 70, wherein said mass is a solid porous mass.

73. The combination of claim 72, wherein said mass comprises zinc particles bound together forming a network of zinc particles with void spaces therebetween.

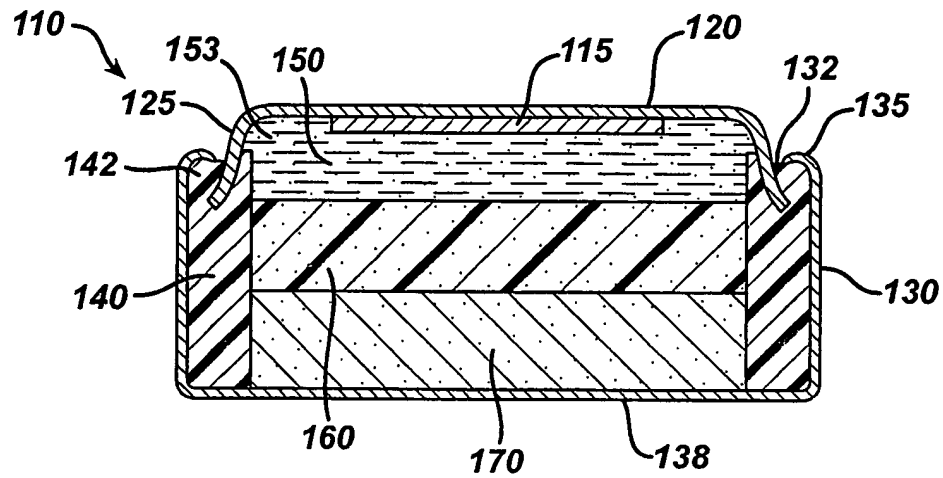
74. The combination of claim 73, wherein said network of bound zinc particles extends at least substantially throughout said mass.

75. The combination of claim 72, wherein said mass has a porosity of between about 25 and 50 percent.

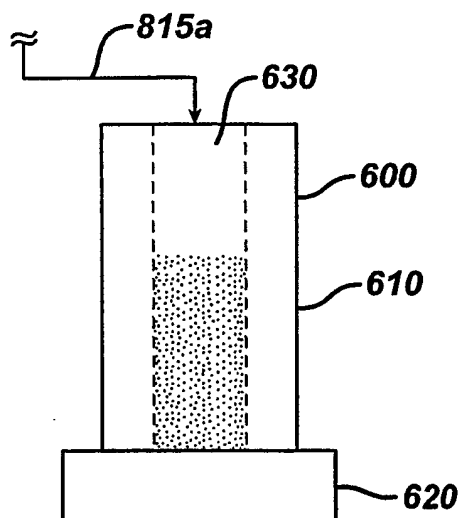
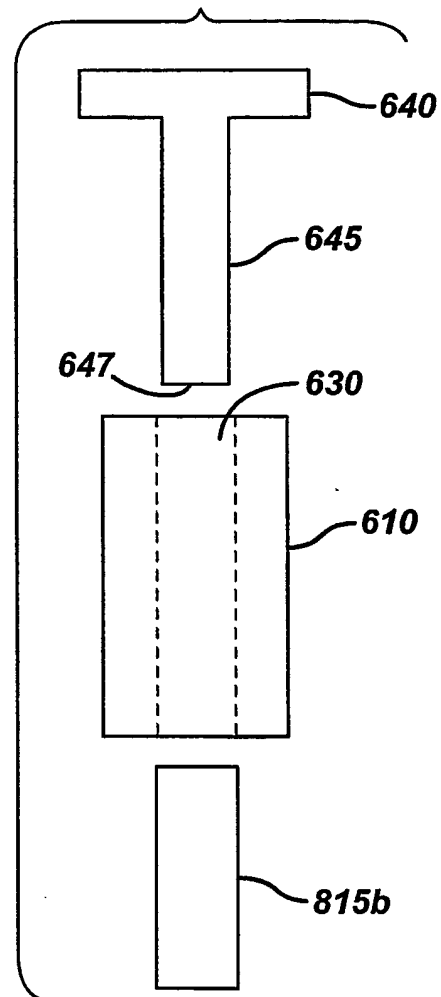
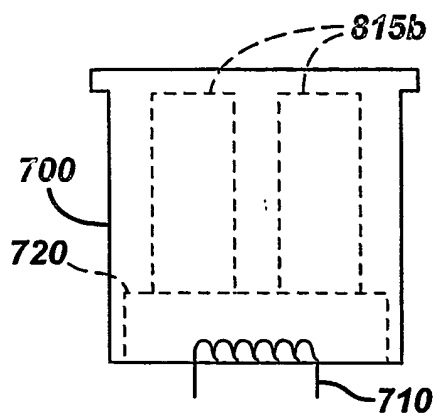
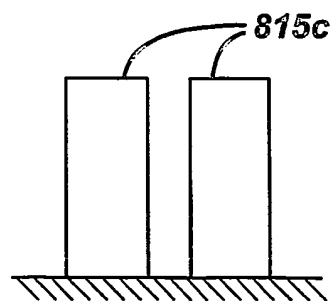
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FIG. 1

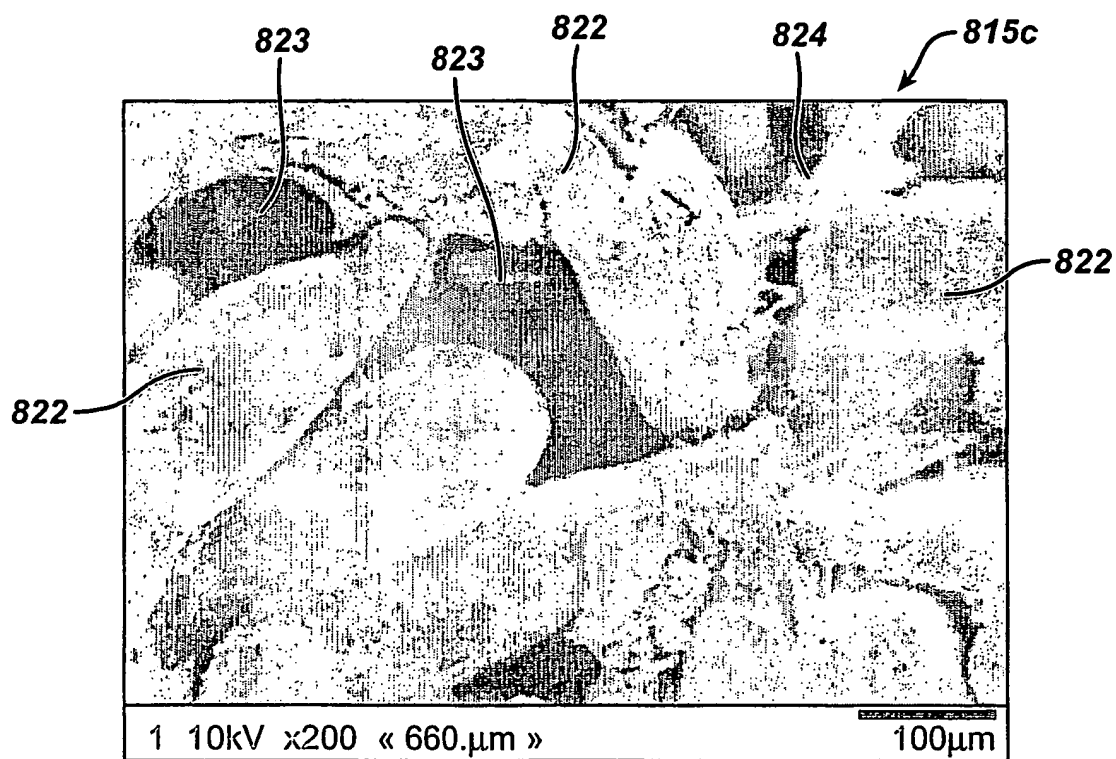
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FIG. 2

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FIG. 3A**FIG. 3B****FIG. 3C****FIG. 3D**

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FIG. 4

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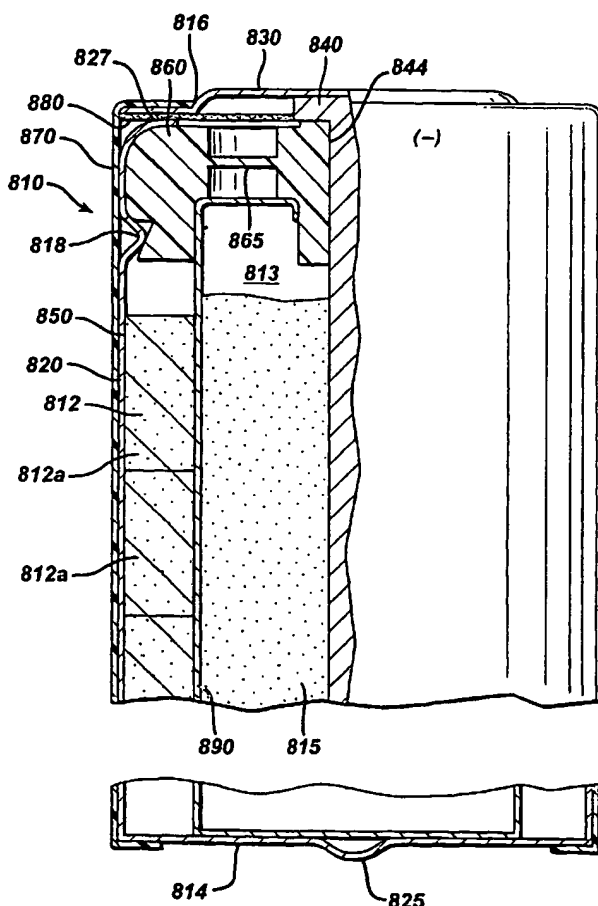
(74) Agents: **CLIFFORD, J.,** Mass et al.; Ladas & Parry LLP, 26 West 61st Street, New York, NY 10023 (US).

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(54) Title: **ALKALINE CELL WITH IMPROVED ANODE**



(57) Abstract: A method of forming an anode comprising zinc for an alkaline cell (810). The method involves mixing zinc particles with binders including preferably polyvinylalcohol, surfactant and water to form a wet paste (815c). The wet paste is molded into the near shape of the cell's anode cavity (813) and then heated to evaporate water. A solid porous zinc mass is formed having microscopic void spaces between the zinc particles. The solid mass can be inserted into the cell's anode cavity and aqueous alkaline electrolyte, preferably comprising potassium hydroxide, then added. The solid mass absorbs the aqueous electrolyte and expands to fill the anode cavity to form the final fresh anode.

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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